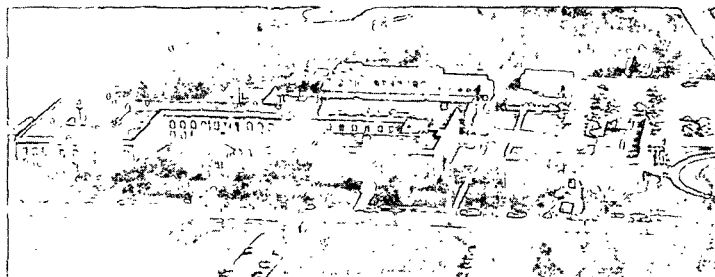


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COLOR REMOVAL IN A FERRIC CHLORIDE-LIME SYSTEM

HARDEV S. DUGAL, JOHN O. CHURCH, ROBERT M. LEEKLEY,  
and JOHN W. SWANSON

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### INTRODUCTION

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Recently, special attention has been given to the effect of pulp and paper mill effluents on receiving water color and to the development of means for reducing the discharge of colored organic material to such waters. Major sources of color from the pulp and paper mill are the caustic extraction stage in bleaching, the unbleached screening and the decker filtrates. Since the major portion of the colored material is highly resistant to microbiological degradation, it passes through the biological treatment processes.

The lime treatment process is currently being used for color removal. About 85-90% of color can be removed in this way. With stricter government regulations on effluent color, better and more efficient ways will have to be found to meet the future standards for the water effluent quality.

This report describes the effect of incorporating certain polyvalent metal ions with lime. It has been shown that over 50% of the color left by the conventional lime treatment process could be removed in this way. The statistical analysis of the data suggests that some interaction between lime and the polyvalent metal ion is present resulting in a better color removal than when either of the two is used separately.

This paper has been submitted to Tappi for publication.

## Color Removal in a Ferric Chloride-Lime System

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### ABSTRACT

It has been shown that over 50% of the color left by the conventional lime treatment processes could be removed by incorporating certain polyvalent metal ions with lime. For example, additions of 100-300 ppm  $\text{FeCl}_3$  with only 300-500 ppm lime removed about 98% color from kraft bleach caustic extract. More color could be removed when the polyvalent metal ions were used with lime than when each was used individually indicating that a "synergistic" effect existed. It was also found that below 1000 ppm of lime, the sludge obtained in this system settled slowly.

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H. S. Dugal, Director, Division of Industrial & Environmental Systems,  
John O. Church, Research Associate, Computer Center, Robert M. Leekley,  
Senior Research Associate and John W. Swanson, Director, Division of  
Natural Materials & Systems, The Institute of Paper Chemistry, Appleton,  
WI.

## Color Removal in a Ferric Chloride-Lime System

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### INTRODUCTION

Color removal is being given special attention because color passes through the biological treatment processes. The lime-treatment process for color removal was developed by the National Council of the Pulp and Paper Industry for Air and Stream Improvement (NCASI) (1-4). This process has gone through the pilot-plant stage and at present is being used by several mills (5-7). Lime precipitation has been shown to remove 85 to 90% of color from the kraft pulping wastes and the addition of larger amounts of lime, above the minimum requirement, does not increase this removal limit.

Recent studies by Dence et al. (8) have shown that the removal of colored material from spent caustic extraction liquor with lime is a chemical rather than a physical process and that color removal is dependent on (a) the presence of enolic and phenolic hydroxyl groups and (b) on the molecular weight of solids contained in the liquor. No data on molecular weight distribution were reported. A more recent study by Dugal et al. (9) has shown that the color bodies which are not removed by lime treatment have an apparent weight average molecular weight of less than 400. These color bodies were shown to contain conjugated carboxyl groups, some ligninlike character and were associated with colorless carbon compounds.

Preliminary studies at the Institute had shown that, by the addition of certain multivalent ions with lime, practically all of the color can be removed. The objective of this work was to establish conditions for such an "improved lime-treatment system."

## RESULTS AND DISCUSSION

Color removal studies were performed on kraft wastes from the decker and the caustic extraction stages of the International Paper Company's mill at Springhill, La. Preliminary experiments were conducted using salts such as barium chloride, ferric chloride, magnesium hydroxide and zinc chloride. Concentrated salt solutions (6000 ppm) were individually prepared and stored for future use. Freeze-dried color bodies from decker and caustic extraction stages were dissolved in distilled water to give 0.1 percent solutions which, eventually, were used for this study. The desired amount of salt solution to give 100-1000 ppm salt per 50 ml total volume was measured into graduated cylinders and filled to the 50-ml mark with the waste to be evaluated. Mixing was accomplished by inverting the cylinders five times. The treated effluent was then allowed to stand undisturbed for a minimum of 15 minutes prior to centrifuging to remove flocculated material. Each treated sample was centrifuged for 15 minutes at 9000 rpm (about 13,000X g). The clear supernatant was carefully poured off and stored until tested for pH and color. The percentage of color removal was calculated and the results are plotted in Fig. 1 through 4. A comparison of Fig. 1 and 2 shows that  $\text{BaCl}_2$  is a better color removing agent for decker wastes than for caustic extract and that among the bivalent ions studied,  $\text{Mg}(\text{OH})_2$  was the least effective.

[Fig. 1 through 4 here]

Based on data from preliminary experiments it was decided to run only the ferric chloride treatment in two series. In one the pH was not adjusted and in the other pH was adjusted to about 9.0 with NaOH to produce a "ferric floc" and then centrifuged (sodium hydroxide was used for pH adjustment to avoid any interference by lime at this stage). Figures 3 and 4 show that  $\text{FeCl}_3$  is more effective for removal of color from caustic extract than from decker waste. An interesting observation is that  $\text{FeCl}_3$  removes more color from decker waste when the pH is not adjusted and is on the acid side. This situation reverses itself in the case of caustic extract. It seems that some decker color was precipitated at lower pH and was removed with the color-Fe complex. In the case of caustic extract, because of higher carboxyl content (10), less color is precipitated at lower pH and, therefore, is not removed. It is, however, taken out with the "ferric floc" under alkaline conditions. The results, in general, show that trivalent ions are more effective color removing agents than the bivalent ions and that a higher percentage of color is removed from caustic extract with  $\text{FeCl}_3$  under alkaline conditions.

Experiments were, therefore, performed to study the effect of lime treatment on kraft bleach effluent in the presence of  $\text{FeCl}_3$ . This study was designed to determine the individual and combined effects of  $\text{FeCl}_3$  and lime on color removal at the following levels of additions.  $\text{FeCl}_3$  was added first to the colored effluent followed by lime.

Lime, ppm: 1000, 2000, 18,000

$\text{FeCl}_3$ , ppm: 0, 25, 50, 100, 200, 300, 500, 800.

The levels of each variable were run once with all levels of the other, giving a total of twenty-four experiments. The results obtained are given in Table 1, and plotted in Fig. 5 and 6. Figure 5 shows that significant

increases in % removal can be realized by using the  $\text{FeCl}_3$ -lime system. This is especially more significant because about 50-80% of color left by the conventional lime treatment process is removed by incorporating these metal ions with lime (10).

[Table 1, Fig. 5 and 6 here]

Figure 6 shows the effect of  $\text{FeCl}_3$  on sludge volume at different levels of lime. Lime concentrations of 1000 and 18,000 ppm at  $\text{FeCl}_3$  concentration of more than 100 ppm give denser sludges than those at 2000 ppm. In fact, sludges obtained with 18,000 ppm lime and more than 100 ppm  $\text{FeCl}_3$ , are the most dense indicating better settling properties.

The color removal data in Table 1 were analyzed using standard regression analysis techniques (11) and a regression equation was obtained:

$$\begin{aligned} \% \text{ removal} = & b_0 + b_1 [\text{FeCl}_3] + b_2 [\text{FeCl}_3]^2 + b_3 [\text{lime}] + \\ & b_4 [\text{lime}]^2 + b_5 [\text{FeCl}_3] [\text{lime}]. \end{aligned}$$

The regression coefficients and their standard errors are shown in Table 2. The specifics and details of this analysis are given elsewhere (10). The last term ( $b_5$ ) in the regression equation indicates a lack of independence between lime and the metal ions and their effect upon the color removal. In other words, it cannot be predicted how much color can be removed by adding 500 ppm  $\text{FeCl}_3$  without also knowing how much lime will be added. Note the intersecting curves in Fig. 7.

[Table 2 and Fig. 7 here]

Using this regression equation and the actual levels of additives, the "calculated" percentage color removal values were obtained and are plotted in Fig. 8. The "actual" values are the color removal values from

Table 1. Figure 8 shows that the agreement between the actual and the calculated data are extremely good for all levels of  $\text{FeCl}_3$  and lime additions.

[Fig. 8 here]

The statistical analysis suggests that some interaction between lime and  $\text{FeCl}_3$  is present resulting in better color removal than when either of the two is used separately. In other words a "synergistic" effect exists.

#### EXPERIMENTAL

##### Color and BOD Measurement

Color and BOD were measured according to the standard methods of the American Public Health Association (APHA) (12). The only modifications of the methods were (1) the use of a noncarbonate buffer for pH adjustment to 7.6 for color measurement and (2) the use of a probe for dissolved oxygen for BOD determinations.

##### Total Organic Carbon (TOC)

The Process Carbonaceous Analyzer (Beckman and Co.) was used for this purpose. Because this instrument gives only total carbon, it was modified to give TOC by the indirect method. One combustion tube was filled with Quartz beads saturated with concentrated phosphoric acid. Total inorganic carbon was first estimated by injecting samples in the  $\text{H}_3\text{PO}_4$ -combustion tube at  $175^\circ\text{C}$ . This tube was then replaced by the regular combustion tube containing the catalyst and total carbon was estimated by injecting samples in catalyst-tube at  $950^\circ\text{C}$ . The difference between total carbon and total inorganic carbon gave TOC.



### Regression Analysis

Regression analysis was performed according to Draper and Smith (11).

### ACKNOWLEDGMENTS

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Mr. J. E. Humphrey, Technical Director, International Paper Company, Springhill, La., supplied the colored effluents.

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REFERENCES

1. National Council of the Pulp & Paper Industry for Air and Stream Improvement (NCASI). Tech. Bull. No. 157, Dec., 1962.
2. Le Compte, A. R., Tappi 49(12):121A, 1966.
3. Berger, H. F. and Brown, R. I., Tappi 42(3):245(1959).
4. Smith, D. R. and Berger, H. F., Tappi 51(10):37A(1968).
5. Davis, C. L., Jr., Tappi 52(11):2132(1969).
6. Spruill, E. L., Water and Sewage Works (Industrial Waste Supplement) 118:15(1971).
7. Humphrey, J. E. Project Director, International Paper Company, Springhill, La., personal communication.
8. Dence, C., et al. NCASI Tech. Bull. 239, 1970.
9. Dugal, H. S., Swanson, J. W., Dickey, E. E., Buchanan, M. A., Tappi 58(7):132(1975).
10. Dugal, H. S., Leekley, R. M., and Swanson, J. W., EPA-660/2-74-029, April, 1974.
11. Draper, N. R., and Smith, H., Applied Regression Analysis, John Wiley & Sons, New York, 1966.
12. Standard Methods, American Public Health Association (APHA). 12th ed., 1965.

Table 1. Lime Treatment of Kraft Bleach Caustic Extract  
in the Presence of Metal Ion

FeCl <sub>3</sub> , ppm	Lime, ppm	Sludge vol., ml	Final pH	Color removal, %	TOC removal, %	BOD removal, %
0	1,000	6.2	11.58	81.4	66.6	6.5
25	1,000	8.2	11.50	81.7	66.0	4.3
50	1,000	8.2	11.42	85.7	71.0	0.0
100	1,000	8.5	11.42	90.0	78.0	12.8
200	1,000	13.3	11.49	91.4	76.4	23.5
300	1,000	14.4	11.50	91.6	74.3	27.7
500	1,000	22.0	11.40	95.8	81.0	36.2
800	1,000	30.1	11.32	95.5	83.2	40.5
0	2,000	6.2	11.79	87.2	68.6	23.5
25	2,000	7.0	11.70	88.0	75.4	23.5
50	2,000	7.3	11.70	89.5	73.0	25.5
100	2,000	9.7	11.70	91.8	75.2	29.8
200	2,000	14.1	11.70	93.6	79.6	34.0
300	2,000	19.1	11.71	95.2	81.6	36.2
500	2,000	33.5	11.78	96.8	86.0	44.7
800	2,000	62.0	11.73	97.5	87.3	51.0
0	18,000	8.9	11.98	93.4	80.4	32.0
25	18,000	8.7	11.99	94.9	79.5	32.0
50	18,000	9.0	11.98	95.0	77.6	38.4
100	18,000	9.4	12.00	95.9	81.7	36.2
200	18,000	11.2	12.01	96.3	84.0	36.2
300	18,000	12.2	12.01	97.3	81.5	46.8
500	18,000	14.3	12.01	98.2	87.7	46.8
800	18,000	16.8	12.00	98.7	88.7	51.0

Note: Untreated caustic extract had pH 8.83, color 4,400 units, TOC 220 mg/l, and BOD 47 mg/l.

Table 2. Effect of Varying Lime and Metal Ion Concentration  
on Color Removal — Regression Coefficients  
and Their Standard Errors

Regression terms	Regression coefficient	Standard error
$b_0$	80.05	--
$b_1$	$35.03 \times 10^{-3}$	$4.239 \times 10^{-3}$
$b_2$	$-0.025 \times 10^{-3}$	$0.00514 \times 10^{-3}$
$b_3$	$3.99 \times 10^{-3}$	$0.8824 \times 10^{-3}$
$b_4$	$-0.0001809 \times 10^{-3}$	$0.000045 \times 10^{-3}$
$b_5$	$-0.0005994 \times 10^{-3}$	$0.000150 \times 10^{-3}$

Note: The regression coefficients  $b_1, b_2, b_3, b_4, b_5$ , give  
the change in the response per unit changes in variable.  
 $b_0$  = Average percentage color removal over the range studied.

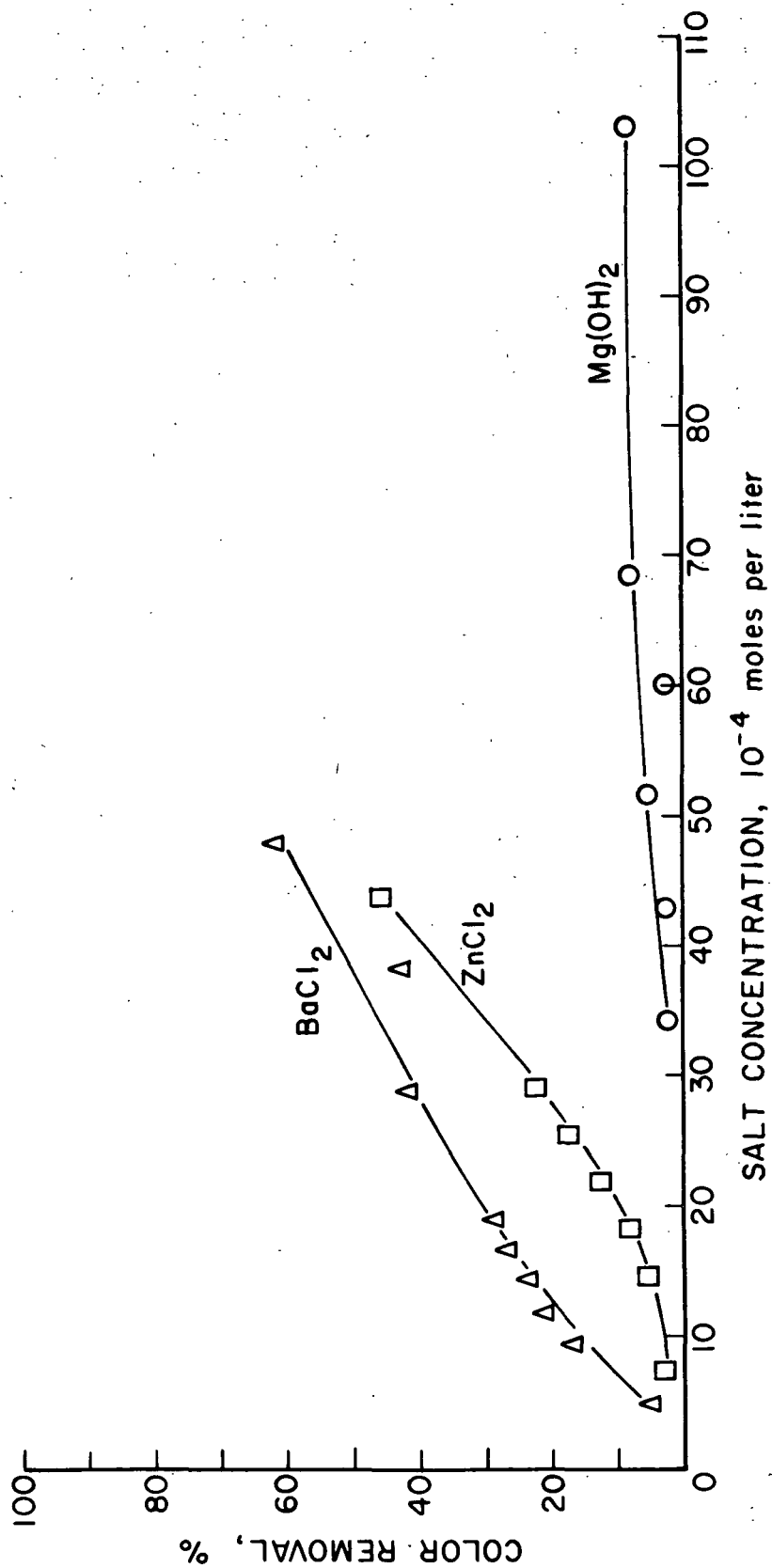


Fig. 1. Treatment of kraft decker wastes with bivalent ions

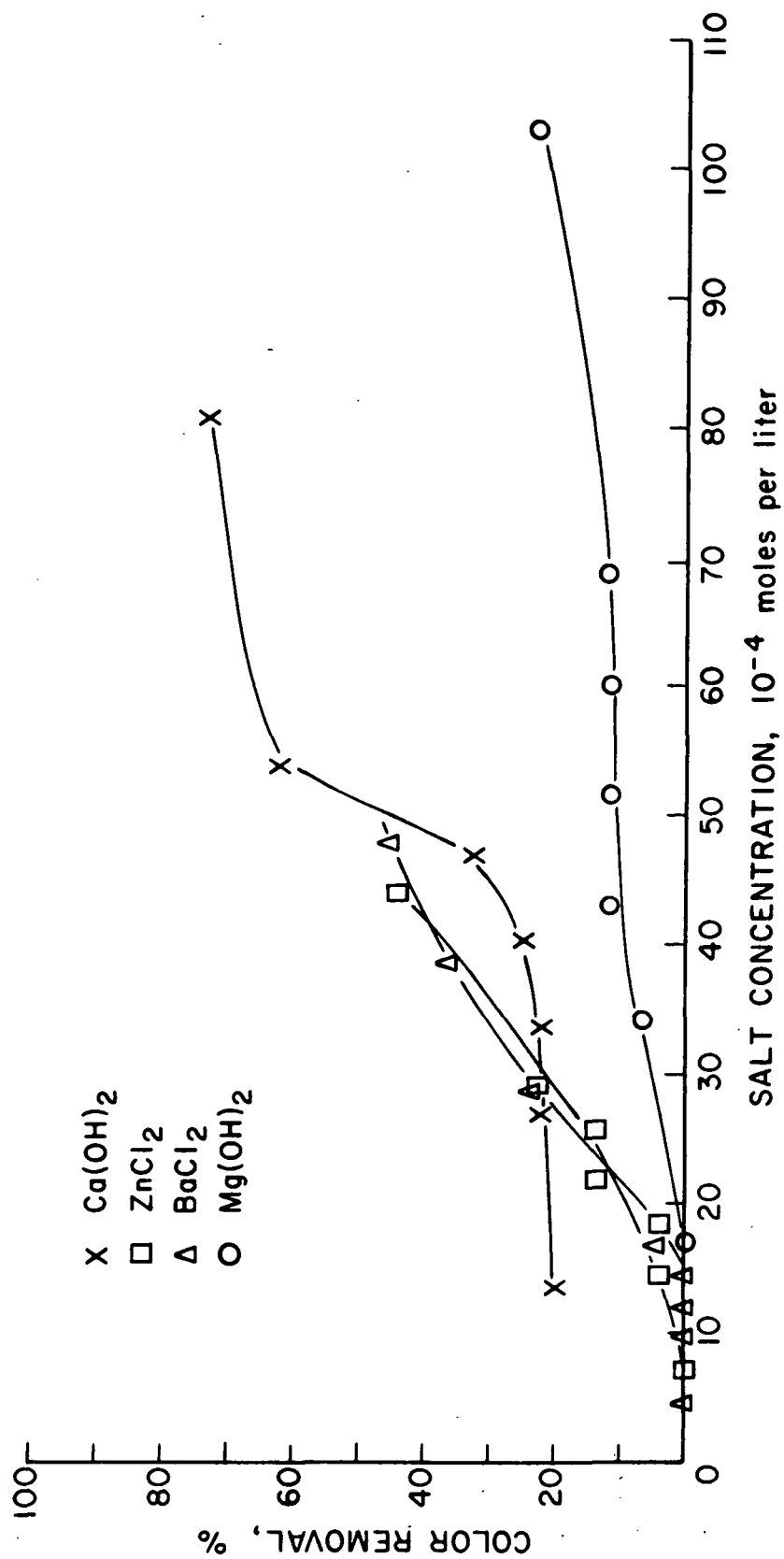


Fig. 2. Treatment of kraft caustic extract with bivalent ions

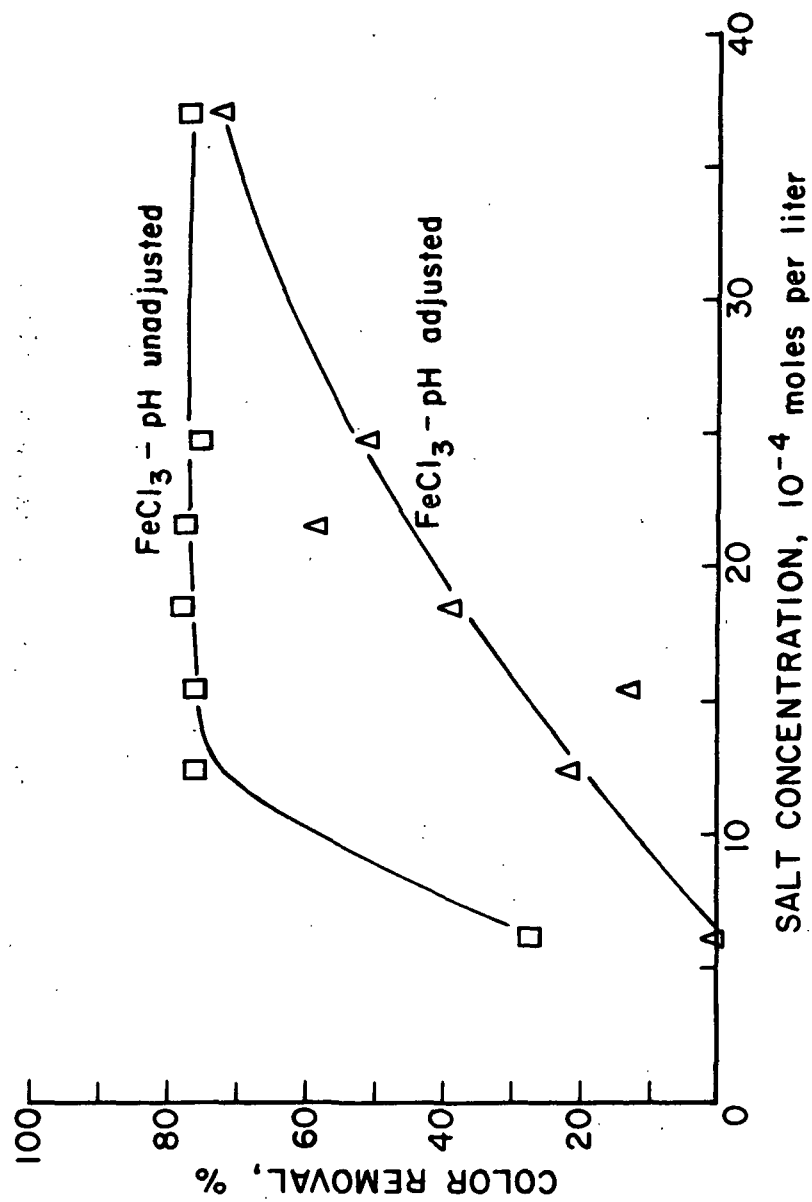


Fig. 3. Treatment of kraft decker waste with trivalent ions

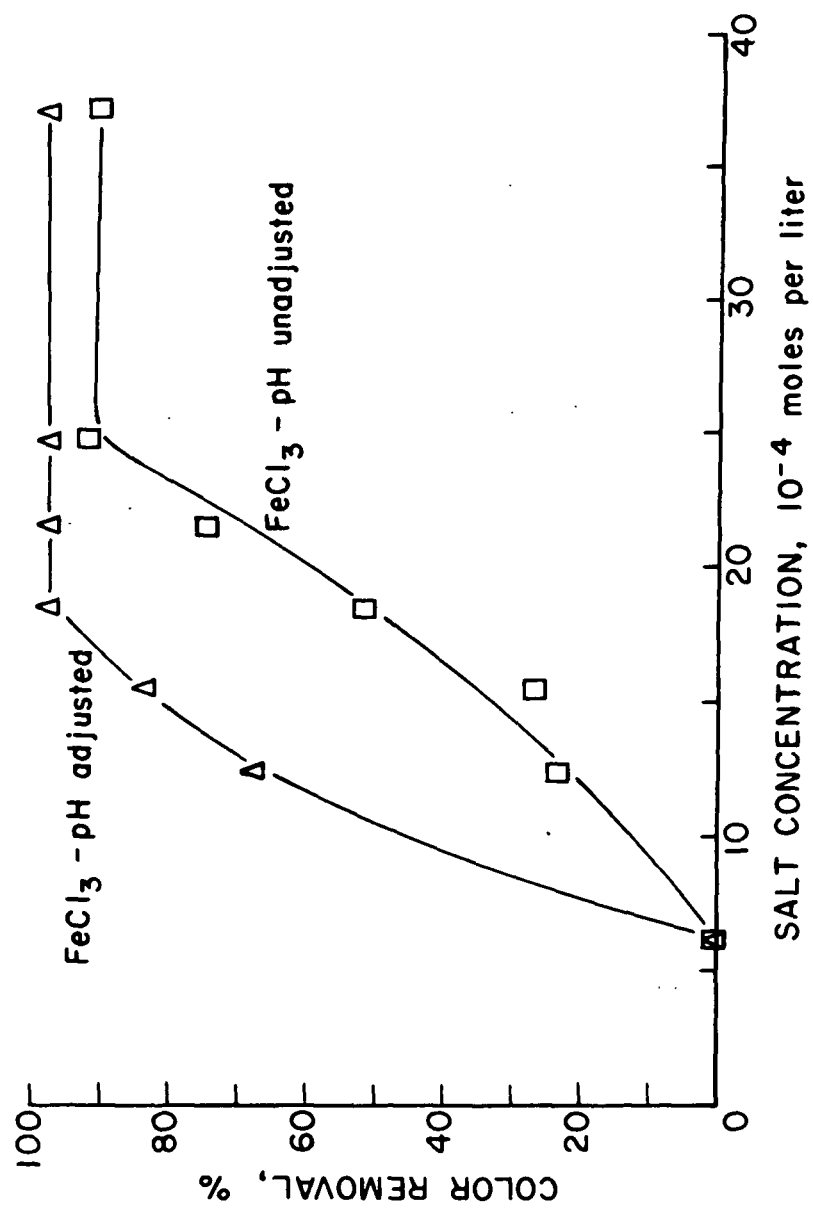


Fig. 4. Treatment of kraft caustic extract with trivalent ions



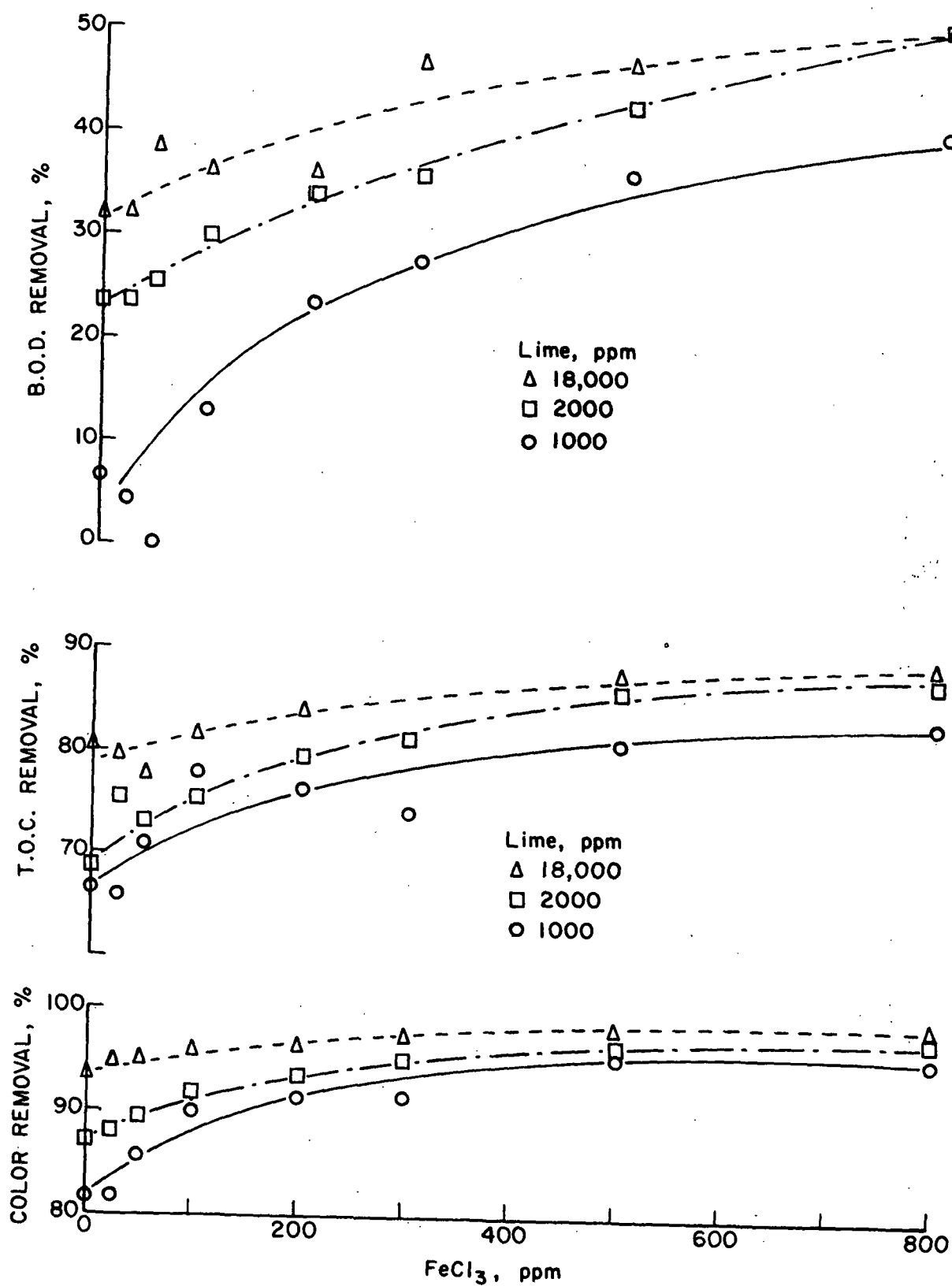


Fig. 5. Effect of  $\text{FeCl}_3$  - lime treatment on color, TOC, and BOD removal (kraft bleach caustic extract waste)

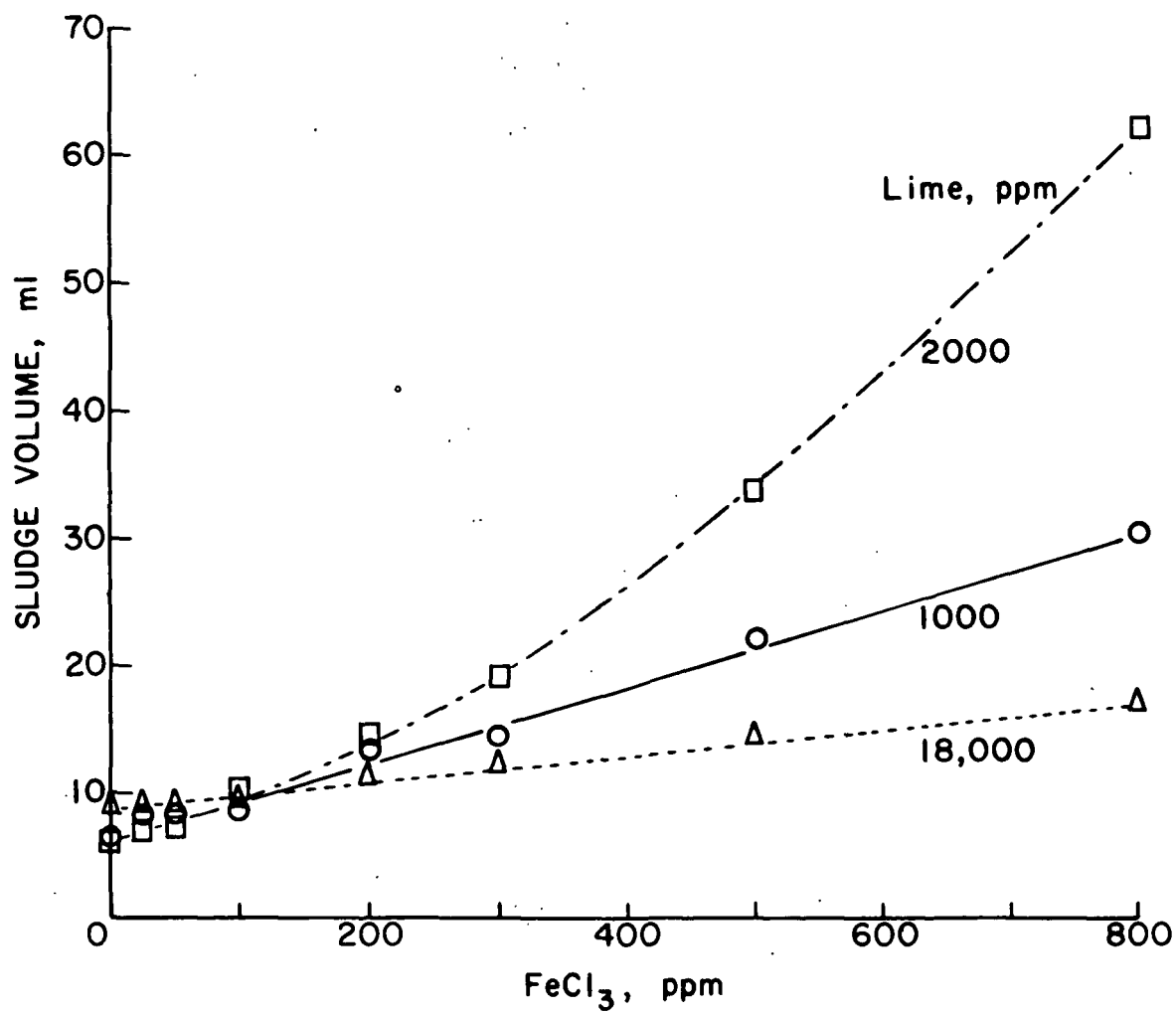


Fig. 6. Effect of ferric chloride and lime on sludge volume (kraft bleach caustic extract waste)

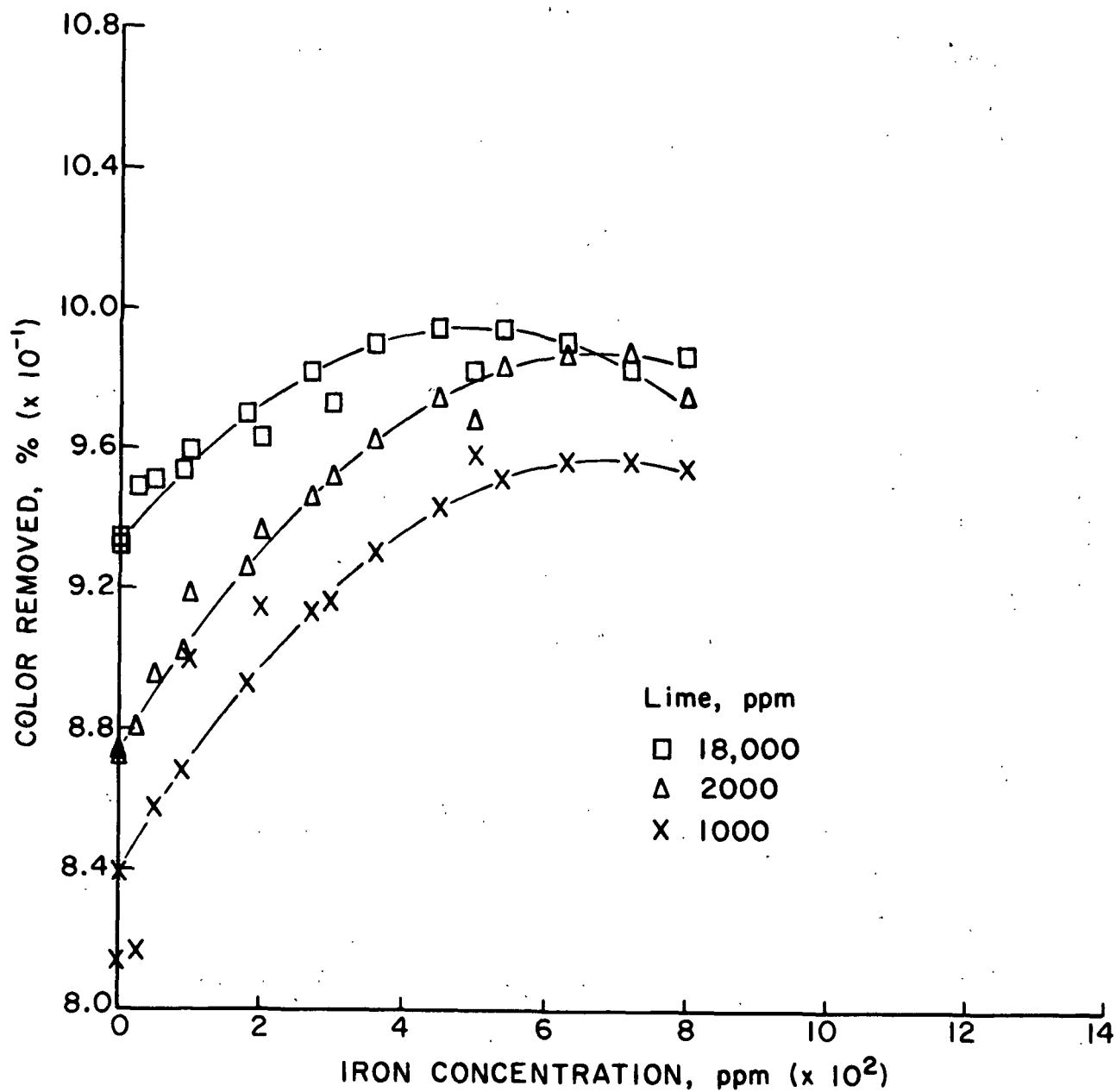


Fig. 7. The interactive behavior of lime and metal ions on color removal (kraft bleach caustic extract waste)

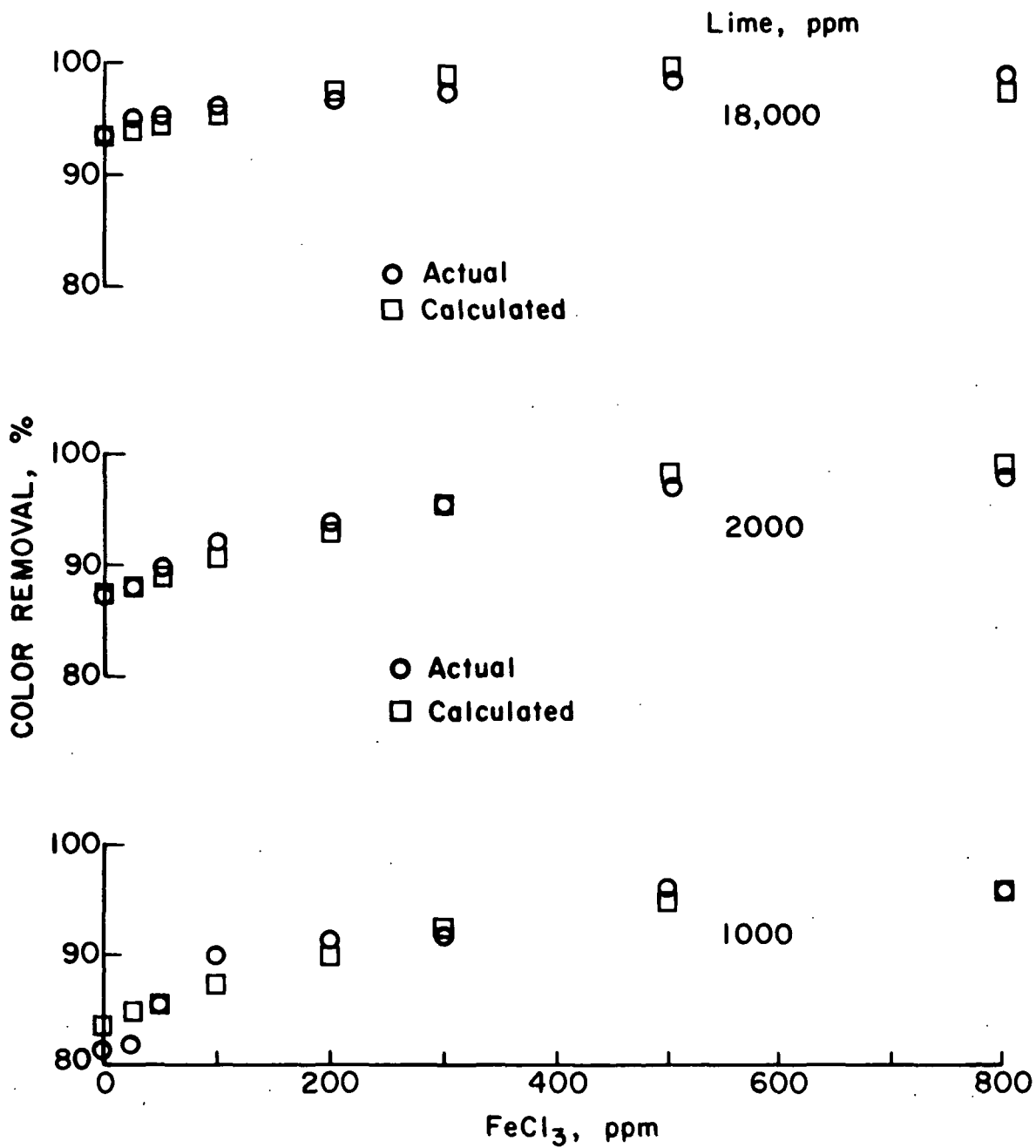


Fig. 8. Percentage of color removal by lime in the presence of metal ions (kraft bleach caustic extract waste)